

APPENDIX D

NOONE-1

MULTI-LAYER FUEL AND VAPOR TUBEI. Field of the Invention:

The present invention relates to a hose for use in a motor vehicle. More particularly, the present invention relates to a multi-layer hose which can be employed as a fuel line or vapor recovery line in a motor vehicle.

II. Background of the Invention:

Single layer fuel lines and vapor return lines of synthetic materials such as polyamides have been proposed and employed in the past. Fuel lines employing such materials generally have lengths of at least several meters. It is important that the line, once installed, not materially change during the length of operation, either by shrinkage or elongation or as a result of the stresses to which the line may be subject during use. It is also becoming increasingly important that the lines employed be essentially impervious to hydrocarbon emissions due to permeation through the tubing. It is anticipated that future Federal regulations will fix the limit for permissible hydrocarbon emissions due to permeation through such lines. A permeation level equal to or below 0.5 g/m² per 24 hour period is required for the lines to meet the new Federal Regulations. Finally, it is also imperative that the fuel line employed be impervious to interaction with corrosive materials present in the fuel such as oxidative agents and surfactants as well as additives such as ethanol and methanol.

Various types of tubing have been proposed to address these concerns. In general, the most successful of these have been co-extruded multi-layer tubing which employ a relatively thick outer layer composed of a material resistant to the exterior environment. The innermost layer is thinner and is

composed of a material which is chosen for its ability to block diffusion of materials such as aliphatic hydrocarbons, alcohols and other materials present in fuel blends, to the outer layer. The materials of choice for the inner layer are polyamides such as Nylon 6, Nylon 6.6, Nylon 11, and Nylon 12.

Alcohol and aromatics in the fluid conveyed through the tube diffuse at different rates through the tubing wall from the aliphatic components. The resulting change in the composition of the liquid in the tubing can change the solubility thresholds of the material so as, for example, to be able to crystallize monomers and oligomers of materials such as Nylon 11 and Nylon 12 into the liquid. The presence of copper ions, which can be picked up from the fuel pump, accelerates this crystallization. The crystallized precipitate can block filters and fuel injectors and collect to limit travel of the fuel-pump or carburetor float as well as build up on critical control surfaces of the fuel pump.

In U.S. Patent Number 5,076,329 to Brunnhofer, a five-layer fuel line is proposed which is composed of a thick outer layer formed of Nylon 11 or Nylon 12, a thick intermediate layer of Nylon 6, and a thin intermediate bonding layer between and bonded to the intermediate and outer layers formed of a polyethylene or a polypropylene. On the interior of the tube is an inner layer of Nylon 6 with a thin intermediate solvent-blocking layer formed of an ethylene-vinyl alcohol copolymer transposed between. The use of Nylon 6 in the inner fluid contacting surface is designed to eliminate at least a portion of the monomer and oligomer dissolution which occurs with Nylon 11 or Nylon 12.

In U.S. Patent Number 5,038,833 to Brunnhofer, a three-layer fuel line is proposed in which a tube is formed having a co-extruded outer wall of Nylon 11 or Nylon 12, an intermediate

alcohol barrier wall formed from an ethylene-vinyl alcohol copolymer, and an inner water-blocking wall formed from a polyamide such as Nylon 11 or Nylon 12. In DE 40 06 870, a fuel line is proposed in which an intermediate solvent barrier layer is formed of unmodified Nylon 6.6 either separately or in combination with blends of polyamide elastomers. The internal layer is also composed of polyamides; preferably modified or unmodified Nylon 6 while the outer layer is composed of either Nylon 6 or Nylon 12.

Another tubing designed to be resistant to alcoholic media is disclosed in UK Application Number 2 204 376 A in which a tube is produced which has an thick outer layer composed of polyamides such as Nylon 6 or 6.6 and/or Nylon 11 or 12 which are co-extruded with an alcohol-resistant polyolefin, a co-polymer of propylene and maleic acid.

Heretofore it has been extremely difficult to obtain satisfactory lamination characteristics between dissimilar polymer layers. Thus all of the multi-layer tubing proposed previously has employed polyamide-based materials in most or all of the multiple layers. While many more effective solvent-resistant chemicals exist, their use in this area is limited due to limited elongation properties, strength and compatibility with Nylon 11 and 12. Additionally, the previous disclosures fail to address or appreciate the phenomenon of electrostatic discharge.

Electrostatic discharge can be defined as the release of electric charge built up or derived from the passage of charged particles through a medium or conduit composed of essentially non-conductive materials. The electrostatic charge is repeatedly replenished with the passage of additional volumes of fuel through the conduit. Discharge repeatedly occurs in the same localized area gradually eroding the area and leading to

eventual rupture leading to the danger of fire and explosion of the flammable contents of the tubing.

Thus it would be desirable to provide a tubing material which could be employed in motor vehicles which would be durable and prevent or reduce permeation of organic materials therethrough. It would also be desirable to provide a tubing material which would be essentially nonreactive with components of the liquid being conveyed therein. Finally, it would be desirable to provide a tubing material which would be capable of preventing the build-up of electrostatic discharge therein or would be capable of safely dissipating any electrostatic charge induced therein.

SUMMARY OF THE INVENTION

The present invention is a multi-layer tube which can be used on motor vehicles for applications such as in a fuel line or a vapor return or recovery line. The tube of the present invention is composed of:

a thick flexible outer tubing having an inner and an outer face, the outer tubing consisting essentially of an extrudable melt processible thermoplastic having an elongation value of at least 150% and an ability to withstand impacts of at least 2 ft/lbs at temperatures below about -20°C;

a thin intermediate bonding layer bonded to the inner face of the thick outer layer, the bonding layer consisting essentially of an extrudable melt processible thermoplastic capable of sufficiently permanent laminar adhesion to the outer tubing; and

an inner hydrocarbon barrier layer bonded to the intermediate bonding layer, the inner layer consisting of an extrudable melt processible thermoplastic capable of sufficiently permanent laminar adhesion with the intermediate bonding layer, the thermoplastic containing as a major constituent a

fluoroplastic selected from the group consisting of polyvinylidene fluoride, polyvinylfluoride, and mixtures thereof.

In the preferred embodiment of this invention, the inner hydrocarbon layer is capable of dissipating electrostatic energy, the electrostatic dissipation capacity being in a range between about 10^{-4} to 10^{-9} ohm/cm².

DESCRIPTION OF THE DRAWING

The objects, features and advantages of the present invention will become more readily apparent from the following description, reference being made to the following drawing in which the Figure is a sectional view through a piece of tubing of the present invention.

DESCRIPTION OF THE PREFERRED EMBODIMENT

The present invention is a multi-layer fuel line and vapor tube which contains at least one bonding layer and at least an outer and an inner tubing layer. The tubing of the present invention is, preferably, fabricated by co-extruding given thermoplastic materials in a conventional co-extrusion process. The tubing may either be co-extruded to a suitable length or may be co-extruded in continuous length and cut to fit the given application subsequently. The tubing of the present invention may have an outer diameter up to 50 mm. However, in applications such as fuel lines and vapor recovery systems, outer diameter of up to 2 inches are preferred.

The material may have any suitable wall thickness desired. However, in automotive systems such as those described herein, wall thicknesses between 0.5 mm and 2 mm are generally employed with wall thicknesses of approximately 0.8 to 1.5 mm being preferred. While it is within the scope of this invention to prepare a tubing material having a plurality of overlaying layers of various thermoplastic materials, the tubing of the present invention generally has a maximum of five layers

inclusive of the bonding layers. In the preferred embodiment, the tubing material has three or four.

5 The tubing 10 of the present invention is a material which is suitable for use in motor vehicles and comprises a relatively thick outer layer 12 which is non-reactive with the external environment and can withstand various shocks, vibrational fatigue, and changes in temperature as well as exposure to various corrosive or degradative compounds to which it would be exposed through the normal course of operation of the motor vehicle.

10 It is anticipated that both the outer tubing layer 12 as well as any interior layers bonded thereto would be suitable for use at an outer service temperature range between about -40°C and about 150°C, with a range of -20°C to 120°C being preferred.

15 The various layers of tubing are integrally laminated to one another and resistant to delamination throughout the lifetime of the tubing. The ^{multi-layer} tubing thus formed will have a tensile strength of no less than 25N per mm square and an elongation value of at least 150%. The tubing will have a burst strength at 23°C and

20 120°C of at least 20 bar. The multi-layer tubing of the present invention is sufficiently resistant to exposure to brake fluid, engine oil and peroxides such as those which may be found in gasoline.

25 The outer layer 12 may be composed of any melt-processible extrudable thermoplastic material which is resistant to ultra violet degradation, extreme changes in heat and exposure to environmental hazards such as zinc chloride, and degradation upon contact with engine oil and brake fluid. In general, the exterior layer is selected from the group consisting of 12 carbon

30 block polyamides, 11 carbon block polyamides as well as zinc chloride resistant 6 carbon block polyamides thermoplastic elastomers. These thermoplastic elastomers are proprietary

compositions and commercially available under tradenames such as SANTOPRENE, KRATON, SARLINK and VICHEM. These materials which compose the outer layers can be present in their unmodified state or can be modified with various plasticizers, flame retardants and the like in manners which would be known to one reasonably skilled in the art.

In the preferred embodiment, a polyamide such as Nylon 12 can be effectively employed. It is anticipated that the Nylon 12 may be either modified or unmodified. If modified, it is anticipated that the material will contain various plasticizers as are readily known in the art.

The Nylon 12 outer layer 16 preferably has a wall thickness between about 0.6 mm and about 0.9 mm with a preferred range being between about 0.7 and about 0.8 mm. As indicated previously, the material is extruded by conventional co-extrusion methods to any continuous length desired.

The inner layer 14 is integrally bonded to the inner surface of the thick outer polyamide layer 12. In the present invention, the inner layer 14 is a completely dissimilar permeation resistant, chemical resistant, fuel resistant thermoplastic material which is melt processible in normal ranges of extrusion, i.e. about 175° to about 250°C. By the term "completely dissimilar" it is meant that the inner layer 14 is a non-polyamide material which is capable of adhesion to a bonding layer interposed between the thick outer layer and the inner layer in a manner which will be described subsequently.

In the preferred embodiment, the thermoplastic material which comprises the inner layer is selected from the group consisting of polyvinylidene, fluoride, polyvinyl fluoride, and mixtures thereof. The preferred material is a polyvinylidene fluoroplastic derived from the thermal dehalogenation of chlorodifluoroethane commercially available under the tradenames

"FLORAFLO" and "KYNAR" from Atochem Inc. of Aquitaine Group of Philadelphia, Pennsylvania.

The thermoplastic material employed in the inner layer is capable of serving as a hydrocarbon barrier to prevent significant permeation of the aromatic and aliphatic components of gasoline through to the polyamide outer layer of the tubing and thus, out to the surrounding environment.

In the preferred embodiment, the inner layer 14 also exhibits conductive characteristics in that it is capable of dissipation of electrostatic charge in the range of 10^{-4} to 10^{-9} ohm/cm². The fluoroplastic material employed in the present invention may be inherently conductive in these ranges or, preferably, includes in its composition a conductive media in sufficient quantity to permit electrostatic dissipation in the range defined. The conductive media may be any suitable material of a composition and shape capable of effecting this static dissipation. The conductive material may be selected from the group consisting of elemental carbon, stainless steel and highly conductive metals such as copper, silver, gold, nickel, silicon and mixtures thereof. The term "elemental carbon" as used herein is employed to describe and include materials commonly referred to as "carbon black". The carbon black can be present in the form of carbon fibers, powders, spheres, and the like.

The amount of conductive material contained in the fluoroplastic is generally limited by considerations of low temperature durability and resistance to the degradative effects of the gasoline or fuel passing through the tubing. In the preferred embodiment, the fluoroplastic material contains conductive material in an amount sufficient to effect electrostatic dissipation. However, the maximum amount employed therein is less than 5% by volume.

The conductive material can either be ^{blended} interstitially integrated into the crystalline structure of the polymer or can be ^{incorporated into the polymer} co-polymerized therewith. Without being bound to any theory, it is believed that carbon-containing materials such as carbon black may be subject to ^{with the polymer} carbon co-polymerization with the ^{fuel} surrounding fluoroplastic material. Material such as stainless steel are more likely to be ^{blended} interstitially integrated into the crystalline structure of the polymer.

The fluoroplastic employed in the inner layer 14 of the present invention is, preferably, completely dissimilar in structure and composition to the outer polyamide layer. In order to accomplish effective lamination of the two dissimilar materials, the tubing of the present invention also includes at least one intermediate layer 16 interposed between the two previously described layers and co-extruded therewith which is capable of achieving a suitable homogeneous bond between itself and the two respective layers. The intermediate bonding layer 16 is generally composed of a more elastic material than that employed in the inner layer.

In the preferred embodiment, the intermediate bonding layer 16 is composed of a thermoplastic material which also exhibits properties of resistance to permeation of aliphatic and aromatic materials such as those found in fuel. The thermoplastic material employed herein is preferably a melt-processible co-extrudable fluoroplastic which may or may not contain various plasticizers and other modifying agents. The intermediate bonding layer 16 is, preferably, a polyvinylidene difluoride polymer, a polyvinyl fluoride polymer, or mixtures thereof which exhibits an affinity to conventional polymers such as Nylon 12 with polyvinylidene fluoride being most preferred. One such polymeric material is commercially available from Atochem under the tradename ADEFLON.

The intermediate bonding layer 16, in addition to permitting a homogeneous bond between the inner and outer layers and exhibiting resistance to permeation of fuel components, also may exhibit conductive or static dissipative characteristics such as those described previously. Thus, the intermediate bonding layer 16 may optionally include sufficient amounts of a conductive media to effect electrostatic dissipation in the range of 10^{-4} to 10^{-9} ohm/cm². As with the inner layer, the intermediate bonding layer may be inherently electrostatically dissipative or may be rendered so by the inclusion of certain conductive material such as those selected from the group consisting of elemental carbon, stainless steel, copper, silver, gold, nickel, silicon and mixtures thereof.

In the preferred embodiment, the inner layer 14 and the bonding layer 16 are maintained at the minimum thickness to prevent permeation of the fuel through the tubing material. It is preferred that the amount of hydrocarbon permeation be no greater than 0.5 grams per meter squared in a 24 hour interval. It is anticipated that the thickness of the inner and intermediate layers can be modified to accomplish this end. In the preferred embodiment, the inner layer has a thickness between about 0.01 mm and about 0.2 mm with a thickness of about 0.05 mm to about 0.17 mm being preferred. The intermediate bonding layer generally may have a thickness less than or equal to that of the inner layer. In general, the intermediate bonding layer has a thickness between about 0.01 mm and about 0.2 mm with a thickness between about 0.05 mm and about 0.15 mm being preferred.

The total wall thickness of the tubing of the present invention is generally between about 0.5 mm and about 2.0 mm with a wall thickness between about 0.8 and about 1.25 mm being preferred.

The tubing of the present invention may also, optionally include an outer jacket (not shown) which surrounds the outer layer. The fourth outer jacket may be either co-extruded with the other layers during the extrusion process or may be put on in a subsequent process such as cross-extrusion. The outer jacket may be made of any material chosen for its structural or insulative characteristics and may be of any suitable wall thickness. In the preferred embodiment, the outer jacket may be made of a thermoplastic material selected from the group consisting of zinc-chloride resistant Nylon 6, Nylon 11, Nylon 12, polypropylene, and thermoplastic elastomers such as SANTOPRENE, KRATON, VICHEM and SARLINK. If desired, these materials may be modified to include flame retardants, plasticizers and the like.

What is claimed is:

1 1. A layered tubing for use in a motor vehicle, the
2 tubing comprising:

3 a thick flexible outer tubing having an inner and an
4 outer face, the outer tubing consisting essentially of an
5 extrudable thermoplastic having an elongation value of at least
6 150% and an ability to withstand impacts of at least 2 ft/lbs at
7 temperatures below about -20°C;

8 a thin intermediate bonding layer bonded to the inner
9 face of the thick outer layer, the bonding layer consisting
10 essentially of an extrudable melt processible thermoplastic
11 capable of sufficiently permanent laminar adhesion to the inner
12 face of the outer tubing; and

13 an inner hydrocarbon barrier layer bonded to the
14 intermediate bonding layer, the inner layer consisting of an
15 extrudable, melt-processible thermoplastic capable of
16 sufficiently permanent laminar adhesion with the intermediate
17 bonding layer, the thermoplastic containing as a major
18 constituent a fluoroplastic selected from the group consisting of
19 polyvinylidene fluoride, polyvinyl fluoride, and mixtures
20 thereof.

1 2. The tubing of claim 1 wherein the inner hydrocarbon
2 barrier layer has is capable of dissipating electrostatic energy,
3 the electrostatic dissipation capacity being in a range between
4 about 10^{-4} to 10^{-9} ohm/cm².

1 3. The tubing of claim 1 wherein the inner hydrocarbon
2 layer contains quantities of a conductive material sufficient to
3 provide electrostatic dissipation capability in a range between
4 about 10^{-4} to 10^{-9} ohm/cm².

1 4. The tubing of claim 3 wherein the conductive
2 material is selected from the group consisting of elemental
3 carbon, copper, silver, gold, nickel, silicon, and mixtures
4 thereof.

1 5. The tubing of claim 4 wherein the conductive
2 material is present in an amount less than about 5% by volume of
3 the polymeric material.

1 6. The tubing of claim 4 wherein the conductive
2 material is interstitially integrated into the milling process
3 fluoroplastic material.

1 7. The tubing of claim 4 wherein the conductive
2 material is elemental carbon and is copolymerized with the
3 extrudable fluoroplastic material.

1 8. The tubing of claim 1 wherein the extrudable
2 thermoplastic of the thick outer tubing is a polyamide selected
3 from the group consisting of Nylon 11, Nylon 12, zinc chloride
4 resistant Nylon 6, Santoprene, Kraton, Vichem, Sarlink and
5 mixtures thereof.

1 9. The tubing of claim 1 wherein the thermoplastic
2 material employed in the intermediate bonding layer exhibits at
3 least some resistance to interaction with short-chain hydrocarbon
4 molecules present in material conveyed through the tubing.

1 10. The tubing of claim 9 wherein the thermoplastic
2 material employed in the intermediate bonding layer includes as a
3 major constituent an extrudable, melt processible fluoroplastic

4 selected from the group consisting of polyvinylidene fluoride,
5 polyvinyl fluoride, and mixtures thereof.

1 11. The tubing of claim 1 further comprising an
2 exterior jacket overlying the thick outer tubing, the exterior
3 jacket composed of a material consisting essentially of a
4 thermoplastic rubber selected from the group consisting of Nylon
5 11, Nylon 12, zinc chloride resistant Nylon 6, Santoprene,
6 Kraton, Vichem, Sarlink and mixtures thereof.

1 12. A layered tubing for use in a motor vehicle, the
2 tubing comprising:

3 an outer tubing having an inner and an outer face, the
4 outer tubing consisting essentially of an extrudable polyamide
5 having an elongation value of at least 150% and an ability to
6 withstand impacts of at least 2 ft/lbs at temperatures below
7 about -20°C;

8 an intermediate bonding layer having a thickness
9 between about 0.01 mm and about 0.2 mm bonded to the inner face
10 of the thick outer layer, the bonding layer consisting
11 essentially of an extrudable thermoplastic capable of
12 sufficiently permanent laminar adhesion to the polyamide outer
13 tubing and exhibiting at least some resistance to short-chain
14 hydrocarbon molecules conveyed through the tubing; and

15 an inner hydrocarbon barrier layer bonded to the
16 intermediate bonding layer having a thickness between about 0.01
17 mm and about 0.2 mm, the inner layer consisting essentially of an
18 extrudable, melt process fluoroplastic capable of sufficiently
19 permanent laminar adhesion with the intermediate bonding layer
20 selected from the group consisting of polyvinylidene fluoride,
21 polyvinyl fluoride, and mixtures thereof.

1 13. The tubing of claim 12 wherein the extrudable
2 thermoplastic of the thick outer tubing is a polyamide selected
3 from the group consisting of Nylon 11, Nylon 12, zinc chloride
4 resistant Nylon 6, and mixtures thereof.

1 14. The tubing of claim 13 further comprising an
2 exterior jacket overlying the thick outer tubing, the exterior
3 jacket composed of a material consisting essentially of a
4 thermoplastic rubber selected from the group consisting of Nylon
5 11, Nylon 12, zinc chloride resistant Nylon 6, Santoprene,
6 Kraton, Vichem, Sarlink, polypropylene and mixtures thereof.

1 15. The tubing of claim 12 wherein the thermoplastic
2 material of the inner hydrocarbon barrier layer is capable of
3 dissipating electrostatic energy, the electrostatic dissipation
4 capacity being in a range between about 10^{-6} to 10^{-9} ohm/cm².

1 16. The tubing of claim 12 wherein the thermoplastic
2 material of the inner hydrocarbon barrier layer contains
3 quantities of a conductive material sufficient to provide
4 electrostatic dissipation capacity in a range between about 10^{-4}
5 to 10^{-9} ohm/cm².

1 17. The tubing of claim 16 wherein the conductive
2 material is selected from the group consisting of elemental
3 carbon, copper, silver, gold, nickel, silicon, and mixtures
4 thereof and is present in an amount less than about 5% by volume
5 of the extrudable thermoplastic material.

1 18. The tubing of claim 16 wherein the conductive
2 material is interstitially integrated into the melt processible
3 fluoroplastic material.

1 19. The tubing of claim 16 wherein the conductive
2 material is elemental carbon and is copolymerized with the
3 extrudable fluoroplastic material.

1 20. The tubing of claim 12 wherein the extrudable
2 thermoplastic of the intermediate bonding layer is a
3 fluoroplastic selected from the group consisting of
4 polyvinylidene fluoride, polyvinyl fluoride, and mixtures
5 thereof.

MULTI-LAYER FUEL AND VAPOR TUBEABSTRACT OF THE DISCLOSURE

5 A layered tubing for use in a motor vehicle composed of
a thick outer tubing having an inner and an outer face, the outer
tubing made of an extrudable thermoplastic such as a polyamide
like Nylon 12; a thin intermediate bonding layer bonded to the
inner face of the thick outer layer, the bonding layer composed
10 of an extrudable melt-processible thermoplastic capable of
sufficiently permanent laminar adhesion to the polyamide outer
tubing; and an inner hydrocarbon barrier layer bonded to the
intermediate bonding layer, the inner layer composed of an
extrudable, melt processible thermoplastic capable of
sufficiently permanent laminar adhesion with the intermediate
15 bonding layer, the thermoplastic containing as a major
constituent a fluoroplastic such as polyvinylidene fluoride,
polyvinyl fluoride, and the like.